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Synthesis of novel tetrathiafulvalene derivatives with thiacrowns

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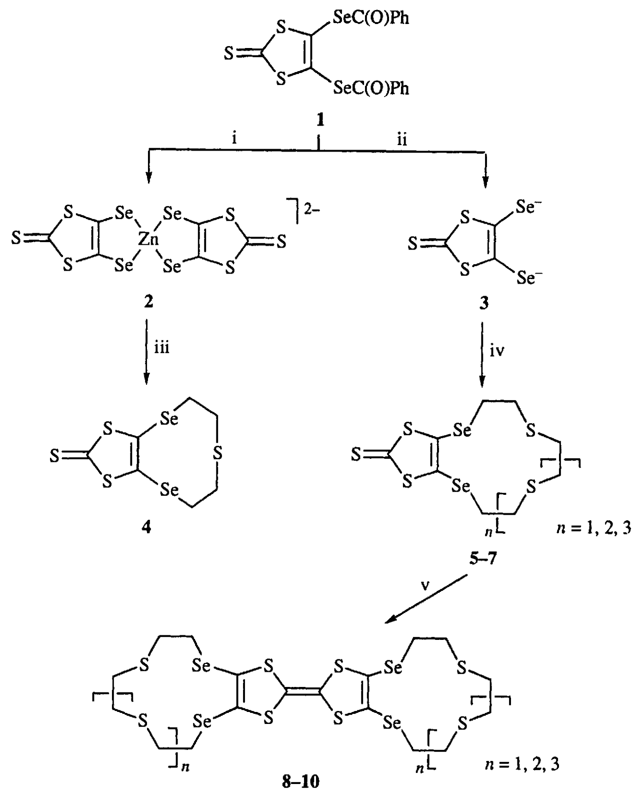
Condensation of dicaesium 2-thioxo-1,3-dithiole-4,5-diselenolate (DSIT) with bis-alkylating polythioethers in high dilution leads to the thiacrown compounds 4–7. On treatment with triethyl phosphite, compounds 5–7 are converted into tetrathiafulvalene derivatives 8–10. The crystal structure of 6, and cyclic voltammograms of the tetrathiafulvalenes 9 and 10, are discussed.

In the field of organic metals the tetrathiafulvalene (TTF) skeleton continues to be one of the most promising. Numerous metal-like charge transfer salts involving electron donors of tetrathiafulvalene type have been prepared.[1] Molecular systems in which the TTF is incorporated into macrocycles with supplementary donor atoms, such as oxygen,[2] nitrogen[3] and sulfur[4] have been investigated in view of their potential use as electroactive cation sensors. Besides the donor atom set and the character of the metal ion (HSAB-concept), the ring size of the macrocycle should be responsible for a changed redox behaviour of the TTF unit.[4,5] We report the synthesis and properties of TTF-containing macrocycles **8–10** with soft donor atoms (sulfur and selenium) and ring sizes of 12, 15 and 18 atoms.

Results and discussion

The key starting material (DSIT) **3** was generated quantitatively from 4,5-bis(benzoylseleno)-1,3-dithiole-2-thione[6] **1** using a method similar to that described for the dicaesium salt of 2-thioxo-1,3-dithiole-4,5-dithiolate (DMIT) (Scheme 1).[3]

When the diselenolate **3** was treated with dialkylating polythioethers in DMF under high dilution conditions, the 1 : 1 adducts **5–7** could be obtained in moderate yields (up to 24%) after purification by chromatography. However, due to the high ring strain in nine-membered rings, the crown compound **4** was isolated only in 3% yield. An improved procedure[7] starting from the zinc chelate **2** gave the strained crown **4** in just over 10% yield. Crystals of **6** suitable for X-ray crystal structure determination were obtained by slow evaporation of a THF solution. The drawing in Fig. 1 and the bond lengths and angles in Table 1 illustrate the molecular geometry of **6** as found in the crystal. The small differences between the bond lengths that involve the chemically equivalent sulfur atoms S12 and S22 could be due to a slight disorder of S12 as indicated by the relatively large displacement parameters for this atom. The other bond lengths and angles correspond closely to those reported previously in thia and selena crown structures.[8] As expected all three of the sulfur atoms point out from the macrocycle. The 18-membered ring might possibly display internal symmetry, but as is shown from the torsion angles listed in Table 1, some noticeable differences exist between the two halves. The moieties C11–Se11–C12–C13–S12 and C21–Se21–C22–C23–S22 are almost related by mirror plane symmetry through C1 and S1, but at S12 and S22 the relation between the fragments S2–C15–C14–S12 and S2–C25–C24–S22 comes closer to twofold symmetry. Se11 and Se21 are almost in the plane of the five-membered ring, which is almost perpendicular to the average plane of the 15-membered ring.



Scheme 1 *Reagents and conditions:* i, $NaOCH_3$, $ZnCl_2$, Et_4NBr, MeOH; ii, CsOH, EtOH, $CHCl_3$; iii, $BrCH_2CH_2SCH_2CH_2Br$, acetone, reflux; iv, $Br(CH_2CH_2S)_nCH_2CH_2Br$, DMF; v, $(EtO)_3P$, 120 °C

Self-coupling of **6** and **7** proceeded cleanly in the presence of neat triethyl phosphite under standard conditions[9] to afford the TTF systems **9** (43%) and **10** (32%), respectively. Under similar conditions the TTF **8** was formed in considerably lower yield (up to 12%) and **4** did not provide the expected tetrathiafulvalene derivative. In contrast to **10**, the TTFs **8** and **9** are insoluble in common solvents, preventing further purification and a more detailed characterization. In addition to elemental analyses of **8–10**, one of the indications of TTF formation was the absence of the intensive thiocarbonyl absorption (at about 1060 cm^{-1}) in their IR spectra. A further proof for the self coupling is the disappearance of the characteristic C=S signal at approximately δ 215 and the appearance of the C=C signal at approximately δ

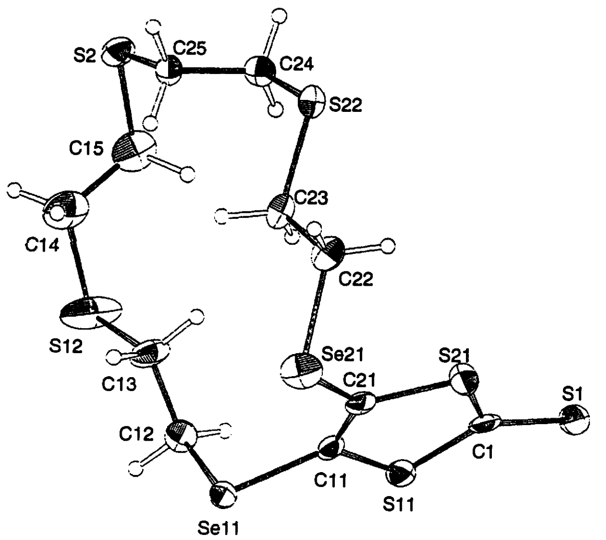


Fig. 1 An ORTEP II[16] drawing of **6** showing the labelling. The thermal ellipsoids for the non-hydrogen atoms enclose 50% probability. The hydrogen atoms are drawn as spheres with fixed radius.

Table 1 Bond lengths, bond and torsion angles in $C_{11}H_{16}S_6Se_2$ **6**

Bond lengths (Å)			
S1–C1	1.648(4)	C11–C21	1.341(6)
C1–S11	1.737(5)	C1–S21	1.709(5)
S11–C11	1.745(5)	S21–C21	1.736(5)
C11–Se11	1.915(5)	C21–Se21	1.905(5)
Se11–C12	1.968(4)	Se21–C22	1.967(5)
C12–C13	1.493(6)	C22–C23	1.498(6)
C13–S12	1.809(5)	C23–S22	1.847(5)
S12–C14	1.844(5)	S22–C24	1.818(5)
C14–C15	1.486(7)	C24–C25	1.505(6)
C15–S2	1.829(5)	C25–S2	1.810(5)
Bond angles (°)			
S11–C1–S21	112.2(2)	C15–S2–C25	99.8(2)
S1–C1–S11	123.9(3)	S1–C1–S21	123.9(3)
C1–S11–C11	97.4(2)	C1–S21–C21	98.5(2)
S11–C11–C21	116.0(4)	S21–C21–C11	115.8(4)
Se11–C11–S11	118.1(3)	Se21–C21–S21	117.8(3)
Se11–C11–C21	125.5(4)	Se21–C21–C11	126.2(4)
C11–Se11–C12	99.3(2)	C21–Se21–C22	98.5(2)
Se11–C12–C13	111.6(3)	Se21–C22–C23	110.7(4)
C12–C13–S12	109.3(4)	C22–C23–S22	108.1(3)
C13–S12–C14	100.7(3)	C23–S22–C24	98.5(2)
S12–C14–C15	110.5(4)	S22–C24–C25	113.0(3)
C14–C15–S2	111.8(4)	C24–C25–S2	112.4(3)
Torsion angles (°)			
C1–S11–C11–Se11	−174.4(3)	C1–S21–C21–Se21	178.0(3)
S11–C11–Se11–C12	−69.6(3)	S21–C21–Se21–C22	55.2(3)
C11–Se11–C12–C13	−82.4(4)	C21–Se21–C22–C23	74.0(4)
Se11–C12–C13–S12	−167.2(3)	Se21–C22–C23–S22	−177.5(2)
C12–C13–S12–C14	−176.5(4)	C22–C23–S22–C24	170.8(3)
C13–S12–C14–C15	86.3(4)	C23–S22–C24–C25	69.4(4)
S12–C14–C15–S2	−172.8(3)	S22–C24–C25–S2	−172.8(3)
C14–C15–S2–C25	89.2(4)	C24–C25–S2–C15	73.4(4)

115 in the ^{13}C NMR spectra. In **6** the high resolution ^{13}C NMR spectrum has been obtained as well as the solid state spectrum. The signal from the C=C bond is present as a doublet in the magic angle spinning (MAS) spectrum of **6** [Fig. 2(*a*)]. The CH_2 signals are spread over only 3 ppm in the high resolution spectrum but cover 20 ppm in MAS spectrum. The spectrum of **9** is very similar but the signal at δ 215.5 has vanished and a signal at δ 110.9 has appeared [Fig. 2(*b*)]. The remaining signals show the same features as for **6**.

The redox behaviour of compounds **9** and **10** was studied by cyclic voltammetry (Fig. 3). Because of its insolubility, the redox potentials of **9** were determined in the solid state using a modified carbon-paste electrode. As expected, **9** exhibits two quasi-reversible redox couples [Fig. 3(*c*)] typical of the TTF system. Under identical conditions, TTF system **10** shows almost the same cyclic voltammogram [Fig. 3(*b*)]. Compared with the reversible redox behaviour of a solution of **10** in CH_2Cl_2 [Fig. 3(*a*)], only the reduction peak potentials are shifted cathodically.

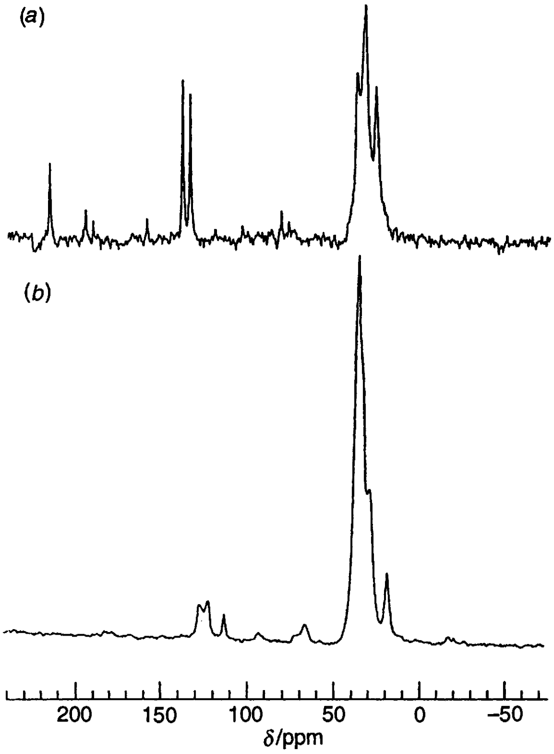


Fig. 2 ^{13}C NMR solid state spectra of (*a*) **6** and (*b*) **9** obtained under CP-MAS conditions. Rotational side bands may be observed in both spectra at RO = 4020 Hz.

Experimental

Spectroscopic measurements

^1H and ^{13}C NMR spectra were recorded on a Varian Unity 500 spectrometer at 499.843 MHz and 125.697 MHz, respectively. The ^{13}C CP-MAS NMR spectra were accumulated on a Bruker MSL 300 spectrometer operating at 75.468 MHz using 2 K data points for accumulation and zero filling to double size prior to Fourier transformation. Magic angle spinning (MAS) spectra were obtained using a Bruker probe HPWB73A and 7 mm PSZ rotors were used with KEL-F end caps. To obtain proper filling the limited amounts of materials were diluted with $NaNO_3$. The cross polarization (CP) conditions were chosen with 2 ms contact to permit all signals to obtain intensity. The chemical shift scale has been adjusted using adamantane as external reference. The mass spectra were obtained on a Varian MAT 311A spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1725 in potassium bromide discs. Cyclic voltammograms were determined on a Schlumberger SI 1286 potentiostat with a platinum counter electrode, Ag/AgCl reference electrode, and a platinum working electrode in a 0.3 M solution of $(Bu_4N)ClO_4$ in CH_2Cl_2. The cyclic voltammograms in the solid state were recorded using the same equipment, with a modified carbon paste working electrode in a 0.3 M solution of $(Bu_4N)ClO_4$ in MeCN. The carbon paste was modified by carefully mixing weighted amounts of the corresponding TTF (**9**: 4.5 mg; **10**: 7.9 mg), carbon powder of spectral grade (42 mg and 68 mg, respectively) and one drop (24 mg) paraffin. This paste was pressed into a Teflon tube (5 mm in diameter) equipped with a central platinum wire.

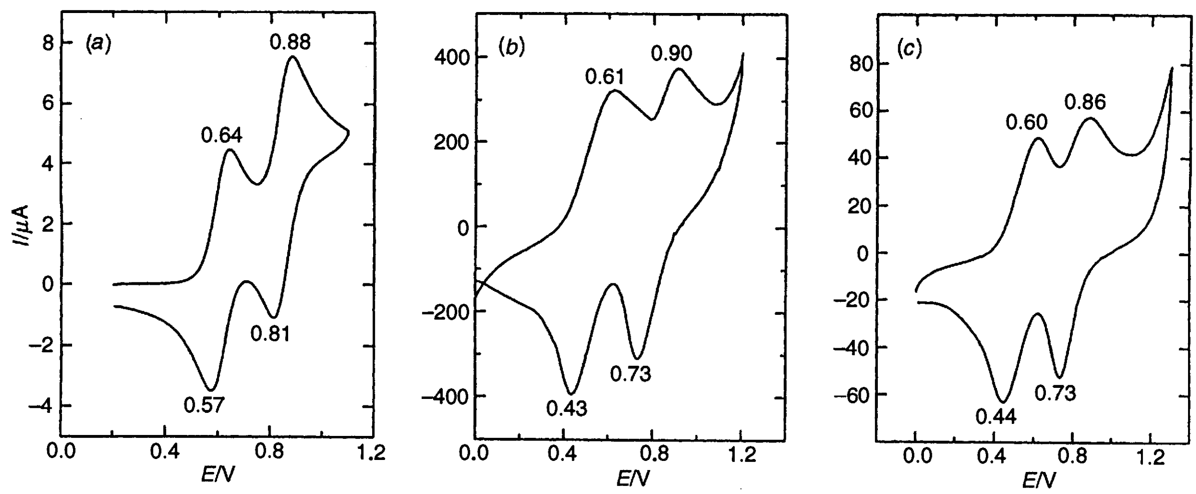


Fig. 3 Solution cyclic voltammogram (CV) of **10** in (*a*) CH_2Cl_2, and solid state CV of (*b*) **10** and (*c*) **9**

Dicaesium 2-thioxo-1,3-dithiole-4,5-diselenolate 3

Starting from 4,5-bis(benzoylseleno)-1,3-dithiole-2-thione **1** a procedure described in ref. 3 was employed to prepare the deep purple salt **3** in quantitative yield (Found: C, 6.31. $C_3Cs_2S_3Se_2$ requires C, 6.48%); δ_C(125.7 MHz; [$^2H_7$]DMF; Me_4Si) 219.6 (*C*=S) and 131.6 (*C*=*C*).

General experimental procedure for compounds 4–7

Into a 250 cm^3 three-necked round-bottom flask equipped with a magnetic stirrer, a gas line to maintain a nitrogen atmosphere, and two Teflon tubes connected with syringes was placed 50 cm^3 DMF. To this neat DMF was added simultaneously a blue solution of the caesium salt **3** (2.78 g, 5 mmol) in 50 cm^3 DMF and a colourless solution of the corresponding dibromide[11] (5 mmol) in 50 cm^3 DMF *via* the syringes at a rate of 2 cm^3 h^{-1} (medical Perfuser pump). After the addition was complete, the brownish mixture was filtered and evaporated to dryness *in vacuo*. The residue was redissolved in CS_2 and separated by preparative layer chromatography (Merck silica gel 60 PF_{254}) with CS_2–CH_2Cl_2 (3 : 2) as eluent. The major yellow band was extracted to yield the desired products **4–7** as yellow solids.

5,10,12-Trithia-2,8-diselenabicyclo[7.3.0]dodeca-1(9)-ene-11-thione 4. (60 mg, 3%), mp 137–139 °C (Found: C, 21.92; H, 2.52. $C_7H_8S_4Se_2$ requires C, 22.22; H, 2.13%); ν_{max}(KBr)/cm^{-1} 2923 (CH_2), 2853 (CH_2) and 1050 (C=S); δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.21 (4 H, t, ^3J 6, C*H*$_2$Se) and 3.09 (4 H, t, ^3J 6, C*H*$_2$S); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 217.6 (*C*=S), 132.2 (*C*=*C*), 34.5 (*C*H$_2$S) and 30.9 (*C*H$_2$Se); *m*/*z* 380 (M$^+$, 40%) and 272 (M$^+$ − C_2H_4Se, 100%); improved procedure for **4**: a stirred solution of tetrabutylammonium bis(2-thioxo-1,3-dithiole-4,5-diselenolato)zincate[6] **2** (4.70 g, 5 mmol) and 2,2′-dibromodiethyl sulfide (2.48 g, 10 mmol) in 150 cm^3 acetone was refluxed for 5 h. Evaporation of the yellow–brown acetone solution yields the crude **4**. Work-up as described above give pure product in 12% yield.

5,8,13,15-Tetrathia-2,11-diselenabicyclo[10.3.0]pentadeca-1(12)-ene-14-thione 5. (270 mg, 12%), mp 178–180 °C (Found: C, 24.75; H, 2.97. $C_9H_{12}S_5Se_2$ requires C, 24.66; H, 2.76%); ν_{max}(KBr)/cm^{-1} 2988 (CH_2), 2890 (CH_2) and 1055 (C=S); δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.27 (4 H, t, ^3J 7, C*H*$_2$Se), 3.06 (4 H, t, ^3J 7, C*H*$_2$S) and 2.90 (4 H, s, C*H*$_2$S); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 215.1 (*C*=S), 128.5 (*C*=*C*), 33.3 (*C*H$_2$S), 32.7 (*C*H$_2$S) and 30.1 (*C*H$_2$Se); *m*/*z* 440 (M$^+$, 100%).

5,8,11,16,18-Pentathia-2,14-diselenabicyclo[13.3.0]octadeca-1(15)-ene-17-thione 6. (600 mg, 24%), mp 149–150 °C (Found: C, 26.50; H, 3.50. $C_{11}H_{16}S_6Se_2$ requires C, 26.50; H, 3.23%); ν_{max}(KBr)/cm^{-1} 2960 (CH_2), 2918 (CH_2) and 1064 (C=S); δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.19 (4 H, t, ^3J 8, C*H*$_2$Se), 3.00 (4 H, t, ^3J 8, C*H*$_2$S) and 2.81 (8 H, s, C*H*$_2$S); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 215.2 (*C*=S), 129.1 (*C*=*C*), 33.1 (*C*H$_2$S), 32.8 (*C*H$_2$S), 32.2 (*C*H$_2$S) and 30.1 (*C*H$_2$Se); δ_C(CP-MAS; 75.47 MHz; $NaNO_3$; adamantane) 215.5 (*C*=S), 138.1 and 133.7 (*C*=*C*), 37.3, 32.6 and 26.2 (*C*H$_2$); *m*/*z* 500 (M$^+$, 60%), 352 (M$^+$ − $C_6H_{12}S_2$, 80%) and 292 (M$^+$ − $C_8H_{16}S_3$, 100%).

5,8,11,14,19,21-Hexathia-2,17-diselenabicyclo[16.3.0]heneicosa-1(18)-ene-20-thione 7. (560 mg, 20%), mp 83–84 °C (Found: C, 28.11; H, 3.64. $C_{13}H_{20}S_7Se_2$ requires C, 27.95; H, 3.61%); ν_{max}(KBr)/cm^{-1} 2902 (CH_2) and 1053 (C=S); δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.19 (4 H, t, ^3J 8, C*H*$_2$Se), 3.01 (4 H, t, ^3J 8, C*H*$_2$S) and 2.83 (12 H, s, C*H*$_2$S); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 214.7 (*C*=S), 128.4 (*C*=*C*), 32.85 (*C*H$_2$S), 32.82 (*C*H$_2$S), 32.7 (*C*H$_2$S), 32.6 (*C*H$_2$S) and 30.0 (*C*H$_2$Se); *m*/*z* 560 (M$^+$, 20%), 292 (M$^+$ − $C_8H_{16}S_3$, 20%), 120 ($C_4H_8S_2$, 90%) and 61 (C_2H_5S, 100%).

General experimental procedure for tetrathiafulvalenes 8–10

The corresponding crown compound (**5**: 88 mg, **6**: 100 mg, **7**: 120 mg; 0.2 mmol) was suspended in triethyl phosphite (5 cm^3), warmed to 120 °C with stirring and the temperature kept constant for 1 h. After cooling to room temperature, the precipitated orange compounds **8–10** were filtered off, washed with methanol and air dried. The soluble tetrathiafulvalene **10** was recrystallized from CH_2Cl_2–MeOH.

14,14′-Bi{5,8,13,15-tetrathia-2,11-diselenabicyclo[10.3.0]-pentadeca-1(12)-en-14-ylidene} 8. (10 mg, 12%), mp > 220 °C (decomp.) (Found: C, 26.22; H, 3.42. $C_{18}H_{24}S_8Se_4$ requires C, 26.60; H, 2.98%); ν_{max}(KBr)/cm^{-1} 2916 (CH_2).

17,17′-Bi{5,8,11,16,18-pentathia-2,14-diselenabicyclo[13.3.0]-octadeca-1(15)-en-17-ylidene} 9. (40 mg, 43%), mp 235–240 °C (decomp.) (Found: C, 28.68; H, 3.89. $C_{22}H_{32}S_{10}Se_4$ requires C, 28.32; H, 3.46%); ν_{max}(KBr)/cm^{-1} 2962 (CH_2) and 2918 (CH_2); δ_C(CP-MAS; 75.5 MHz; $NaNO_3$; adamantane) 125.2 and 120.4 [Se*C*(S)=*C*(S)Se], 110.9 [S*C*(S)=(S)*C*S], 35.8, 28.3 and 17.2 (*C*H$_2$).

20,20′-Bi{5,8,11,14,19,21-hexathia-2,17-diselenabicyclo-[16.3.0]heneicosa-1(18)-en-20-ylidene} 10. (34 mg, 32%), mp 153–155 °C (Found: C, 30.32; H, 4.26. $C_{26}H_{40}S_{12}Se_4$ requires C, 29.65; H, 3.83%); ν_{max}(KBr)/cm^{-1} 2904 (CH_2); δ_H(500 MHz; $CDCl_3$; Me_4Si) 3.11 (8 H, t, ^3J 8, C*H*$_2$Se), 2.95 (8 H, t, ^3J 8, C*H*$_2$S), 2.82 (16 H, s, C*H*$_2$S) and 2.79 (8 H, s, C*H*$_2$S); δ_C(125.7 MHz; $CDCl_3$; Me_4Si) 120.1 [Se*C*(S)=(S)*C*Se], 113.3 [S*C*(S)=(S)*C*S], 32.8 (*C*H$_2$S), 32.7 (*C*H$_2$S), 32.6 (*C*H$_2$S), 32.4 (*C*H$_2$S) and 29.1 (*C*H$_2$Se).

X-Ray crystallography

A single crystal, 0.35 × 0.2 × 0.1 mm was selected from the sample of red needle-shaped crystals of **6**. An Enraf-Nonius CAD4 diffractometer was used for the data collection. The cell

Table 2 Crystal data and structure refinement for $C_{11}H_{16}S_6Se_2$ **6**

Empirical formula	$C_{11}H_{16}S_6Se_2$
M_r/g mol^{-1}	498.52
Radiation	Mo-Kα (λ = 0.710 73 Å)
T/K	122.0(5)
Space group	$P\bar{4}2_1c$
Cell parameters at 122 K	
a/Å	19.341(4)
c/Å	9.647(2)
V/Å^3	3608.7(13)
Z	8
D_x/g cm^{-3}	1.835
Linear absorption coefficient μ/mm^{-1}	4.777
Data collection	
θ Range/°	1–30
Octants measured	$hk \pm l$
Number of measured reflections	6144
Number of independent reflections	2920 (R_{int} = 0.032)
Number of observed reflections $\lvert F\rvert^2 > 2\sigma(\lvert F\rvert^2)$ $w = \frac{1}{\sigma^2}(\lvert F\rvert^2)$	2346
Refinement	
$R[F^2 > 2\sigma(\lvert F\rvert^2)]$	0.040
$wR(\lvert F\rvert^2)^a$	0.0520
S	1.601
Number of parameters	172
Number of contributing reflections	2915

^{a} $wR(|F|^2) = \left\{\frac{\Sigma w(|F_o|^2 - |F_c|^2)^2}{\Sigma w|F_o|^2}\right\}^{\frac{1}{2}}$; $w = \frac{1}{\sigma^2(|F|^2)}$.

parameters and orientation matrix were determined from the least-squares refinement of the setting angle of 20 reflections with θ in the range 17–22°. The crystal data and a summary of results from the data reduction and structure refinement are listed in Table 2. The data reduction was performed with the DREADD[12] program package. Reflections related by the symmetry of the crystal class were averaged.

The structure was solved by a combination of Patterson and direct methods using SHELXS-86.[13] SHELXL-93[14] was used for the structure refinement. The absolute structure was determined as described by Flack[15] and the corresponding parameter refined to −0.018(11).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/38.

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